ORIGINAL PAPER

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A composite proton-conducting membrane based on a poly(vinylidene)fluoride-poly(acrylonitrile), PVdF-PAN blend

Abstract This paper reports on the synthesis and the properties of a new microporous, composite proton-conducting gel membrane, formed by swelling a poly(vinylidene)fluoride- poly(acrylonitrile), PVdF-PAN blend-based matrix containing a dispersed Al_2O_3 ceramic filler with aqueous acid solutions. We show that this membrane has a high and stable conductivity, a proton transport not critically influenced by the relative humidity level, and a projected low cost. Tests in a methanol-air laboratory cell also demonstrate that the membrane is basically suitable for application in direct methanol fuel cells.

Keywords Membrane · Proton conductivity · Fuel cells

Introduction

Due to their relevance to emerging fuel cell technologies, proton-conducting polymer electrolytes are presently being widely studied. The most common and established types are the perfluorinated membranes, of which Nafion is a typical example [1]. Indeed, Nafion and related perfluorinated polymers are still the electrolyte membranes of choice for fuel cells of interest as power sources for electric vehicles, stationary applications and portable electronics. However, although having favorable properties, these perfluorinated membranes are not yet ideal since they have a few important drawbacks, such as high cost, low thermal stability, and low selectivity for fuel permeability. In addition, in order to acquire sufficient proton conductivity, Nafion (and the perfluorinated membranes in general) requires the presence of liquid water [2]. Although water is a product of the electrochemical process, it is not always easy to keep the membrane properly soaked, and so water management is still a critical issue for practical fuel cells.

All of this has prompted significant research activity aimed at the development of alternative membranes characterized by: i) a high protonic conductivity that is not as critically dependent on the water content as in the perfluorinated case; ii) chemical stability, and; iii) low cost. Many attempts have been made to synthesize modified perfluorinated systems with improved thermal stability combined with high conductivity and low cost [1, 3], although with limited progress.

Different, new-concept, approaches must then be sought to obtain alternative types of proton conducting membranes. One promising area of development is in the field of so-called "gel-type polymer electrolytes", prepared by readapting synthesis procedures which have proved successful in the lithium polymer technology [4]. Basically, this approach consists of swelling a polymer matrix with proton-conducting liquid solutions [5]. There are two types of gel-type polymer electrodes, which differ in the type of swelling solvent: "aqueous gels", when an acid (for instance H_3PO_4 or H_2SO_4) aqueous solution is used, and "nonaqueous gels" when a solution of a strong acid (like trifluoroacetic acid) in a highly polar solvent (such as ethylene carbonate-propylene carbonate, EC-PC solvent mixture) is used. While the latter type may also have interesting applications in other types of devices beyond fuel cells (like electrochromic windows [6], supercapacitors [7], and photoelectrochemical cells [8]), it is the aqueous gel type that has the most potential for application in fuel cells.

The original idea for the gel approach to fuel cell technology was proposed by Peled and co-workers, who reported on a poly(vinylidene)fluoride, PVdF-based porous membrane filled by aqueous acid solutions [9], and on its successful application in a direct methanol fuel cell, DMFC [10]. We have extended this concept to a series of new types of gel membranes, including: i) poly(methyl methacrylate), PMMA-based membranes swollen by solutions of salicylic or benzoic acid in a

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EC-PC mixture [11, 12]; ii) poly(acrylonitrile), PAN-based membranes swollen by solutions of trifluoroacetic acid in EC-PC solvent mixture [13], and; iii) poly(vinylidene)fluoride, PVdF-based membranes swollen by an aqueous solution of sulfuric acid [14]. In this work we extend the series by describing the synthesis and the characteristics of a composite PAN-PVdF blend-based membrane containing a dispersed Al_2O_3 ceramic filler swollen by aqueous acid solutions.

Experimental

In the approach followed in this work, the proton-conducting membranes were prepared in two main steps. First, a self-standing, porous polymer matrix was prepared. Then this "precursor" matrix was swollen with an aqueous acid solution to obtain the final proton conductor. The precursor membrane was prepared using a blend of Kynar 2801 PVdF (100,000 molecular weight and 11–12% of HFP copolymer, Degussa) and PAN (150,000 average molecular weight, Aldrich), in a 1:1 weight ratio. Al_2O_3 ceramic powder (300 nm sized, Aldrich) was added to the polymer blend and the components were intimately mixed. The resulting mixture was then dispersed in a cyclopentanone-propylene carbonate, CP:PC (3:7 molar ratio) solvent mixture by continuous stirring, to obtain a slurry which was poured into a Petri glass substrate. The forming process was performed by first heating the slurry at 90 °C and then quenching it. Among the various compositions tested, the one having a CP:PC-PVdF-PAN-Al2O3, 76-7-7-10 weight% ratio was identified as the most appropriate. This selected precursor membrane was washed in distilled water to remove the CP-PC solvent mixture and

then swollen at 100 °C using a 6 M H_2SO_4 aqueous solution to obtain the final, proton-conducting membrane.

The thermal properties of the membrane were investigated by Thermal Gravimetric Analysis (TGA) run with a Perkin Elmer TGA7 thermobalance in air atmosphere, at a heating rate of 5 °C/min and over a temperature range of 20–180 °C. The thermobalance was coupled with a Perkin Elmer FTIR spectrometer, model 1760X, in order to obtain the in situ IR spectra of the gases that were evolved during the analysis. Morphological investigations of the membranes were performed by scanning electron microscopy, SEM, using a LEO 1450 VP apparatus.

The ionic conductivity was determined from impedance spectra obtained on a cell formed by sandwiching a sample of the given swollen membrane between two platinum electrodes using a Solartron 1255B frequency response analyzer under computer control. In order to investigate the role of humidity in the transport properties, the measurements were carried out in a water atmosphere, by placing the cell either in a water-saturated container or in anhydrous conditions, and by keeping the cell in an environmentally-controlled dry box.

The practical use of the membrane was evaluated by determining the current-voltage curves of an in-house made, two-electrode fuel cell consisting of two gas distribution titanium nets in contact with the carbon-electrocatalyst-based gas electrodes and the selected membrane in-between. The gas electrodes were prepared by loading a carbon-PVdF membrane with the platinum catalyst at 3.2 mg cm^{-2} load. The geometric area of the electrode was estimated at 1.13 cm^2, and the membrane thickness was of the order of 300 μm. The cell contained

Fig. 1 SEM image of a Al_2O_3-added, composite PAN-PVdF blend membrane
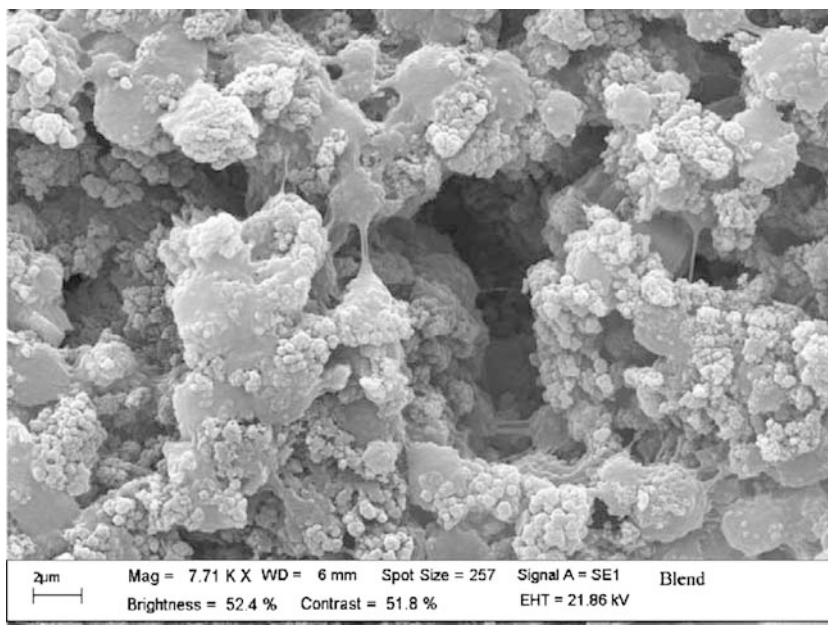
inlets through which the anode was supplied with 2 M methanol acidic solution and the cathode was supplied with air, the latter at constant flux via a water bubbler.

Results and discussion

The syntheses of the protonic membranes reported in this work depend on the initial formation of a ceramic-added composite obtained by the gelification of a poly(acrylonitrile), PAN-poly(vinylidene)fluoride, PVdF-blend polymer matrix. This precursor matrix is then soaked in an acidic solution to promote a liquid phase inversion process, during which the CP:PC gelling solvent mixture partially leaves the polymer matrix to be replaced by the H_2SO_4 aqueous acid solution, to finally obtain self-standing, highly proton-conducting membranes.

The liquid exchange is a key step in ensuring proper membrane functionality. In this respect, the optimization of the porosity of the host polymer matrix is an important factor. A suitable porosity can be promoted by controlling the crystallinity of the polymer, say by using suitable polymer blends, such as the PAN-PVdF selected here. The dispersion of nanoparticle-sized ceramic powders in the polymer mass is also beneficial. Indeed, it is expected that the ceramic fillers may induce formation of micropores in the polymer matrix by interrupting the chain sequence via the promotion of Lewis acid-basic interactions with the PAN component. In addition, ceramics such as SiO_2 or Al_2O_3, due to their affinity for water, act as liquid-absorbing centers, which promotes liquid uptake and retention in the membrane. The beneficial effects from dispersed fillers in promoting robustness and conductivity has been demonstrated for various cases, including those involving "conventional" Nafion-type membranes [15].

The SEM investigation confirms the beneficial action of the PAN component and of the dispersed filler. As clearly shown by the SEM image of Fig. 1, the PAN-PVdF-Al_2O_3 blend membrane is characterized by an extended porosity and by a series of intersecting cavities of few microns in size. It is in fact the presence of PAN which confers this appropriate morphology, since membranes based on PVdF alone have a compact, plastic-like morphology [14]. A contribution to porosity enhancement is also provided by the dispersed nano-particle size ceramic powders. These powders, due to their hydrophillicity, act as liquid-absorbing centers, promoting liquid uptake and retention in the membrane without adversely affecting its mechanical properties.

The favorable characteristics of the Al_2O_3-added, composite PAN-PVdF- based membranes are confirmed by thermal analysis, see Fig. 2. The TGA response of an acid-swollen membrane reveals a total mass loss of about 25% over a 20–180 °C temperature range, Fig. 2A. The derivative curve shows the presence of three different releasing phenomena, as revealed by: i) a smooth shoulder up to 100 °C; ii) a well-defined valley between 100–130 °C, and; iii) a sluggish valley in the
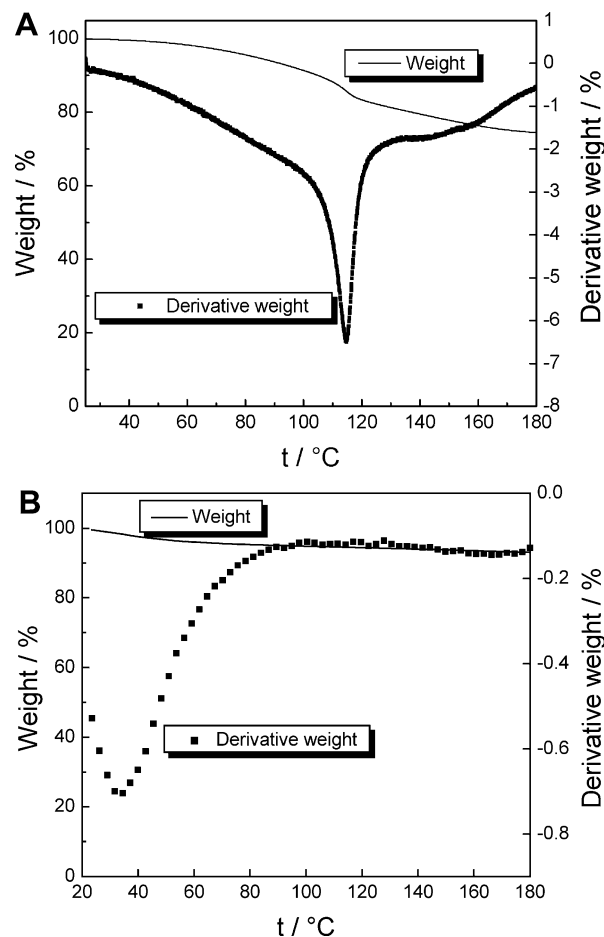

Fig. 2 TGA curves for a PAN-PVdF-Al_2O_3 composite membrane swollen by a 6 M H_2SO_4 aqueous solution (A) and for a Nafion 117 membrane soaked with HNO3 (10% vol) (B). Scanning rate: 5 °C/min. Air flux

final temperature range. The in situ IR analysis of the products formed by the thermal decomposition revealed that water was the only component released during the whole temperature scan. On the basis of this evidence, we suggest that the first thermal process (up to 100 °C) indicates a removal of the surface-adsorbed water, while process (ii) around 115 °C reflects the release of bulk water, and process (iii) in the 130–180 °C region is probably associated with the release of bonded water, such as that coordinated by the Al_2O_3 filler and/or by the H_2SO_4 component. It is worth pointing out that, up to 100 °C, the water release process is slow, conferring a practical value to the membrane. Figure 2B shows for comparison purpose the TGA response of a conventional Nafion 117 membrane, activated by a 10% vol HNO_3 aqueous solution. Although the mass loss is less than that observed with the PAN-PVdF-based membrane (8% versus 25%), the water release occurs at lower temperatures (40 °C versus 115 °C). In conclusion, we stress the fundamental role played by the ceramic filler, which contributes not only to assure liquid retention and but also thermal stability to the composite
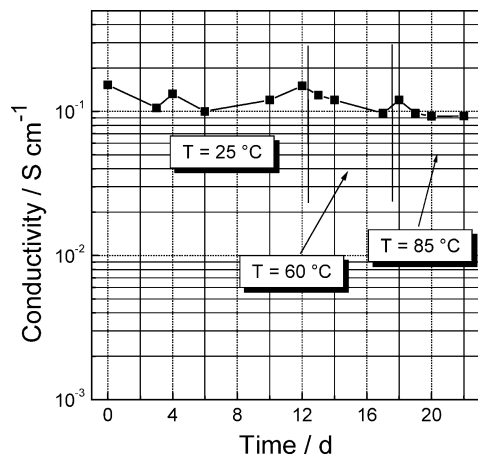
Fig. 3 Conductivity versus storage time at different temperatures for a PAN-PVdF-Al$_2$O$_3$ composite membrane swelled by a 6 M H$_2$SO$_4$ aqueous solution. Relative humidity ~100%

polymer membrane. In addition, the filler is quite beneficial in promoting the robustness of the polymer membranes.

Figure 3 shows the time evolution of the conductivity of the PAN-PVdF-based membrane measured at progressively increasing temperatures. The conductivity at 25 °C is considerably high, averaging a value of 0.1 S cm^{-1}. The conductivity also remains high and stable at higher temperatures, up to 85 °C, confirming the membrane's favorable thermal characteristics as already evidenced by the TGA response, see Fig. 2A.

The conductivity mechanism of these gel-type membranes is substantially different form that occurring in Nafion-type systems, where the presence of water is vital for assisting the proton transport. Although further work, like that based on spectroscopic measurements, is certainly needed to reach definite conclusions, we may
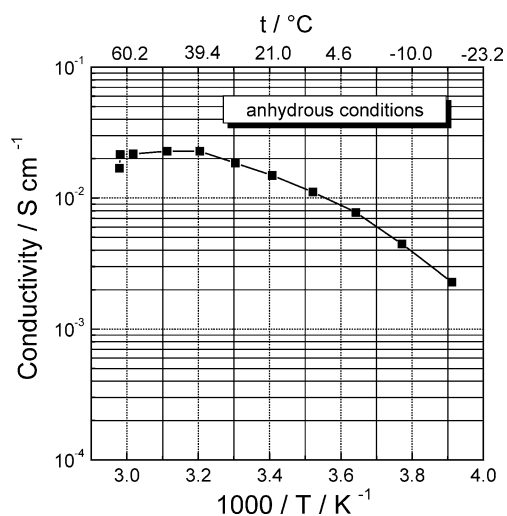
assume that in the membranes considered in this work the proton transport is intrinsically assured by the swollen acid solution, and so the conductivity is expected to be less dependent on the external relative humidity. Figure 4 shows a conductivity Arrhenius plot of a swollen PAN-PVdF composite membrane measured in anhydrous conditions, by keeping the cell in a dry box with a water content less than 1 ppm. Although lower that those detected in the presence of humidity, the conductivity values are still of the order of 0.01 S cm^{-1} at room temperature. This confirms that the PAN-PVdF gel membrane may also give reasonable protonic transport in dry environments and at temperatures as low as −20 °C. Note that Nafion-type membranes are practically non-conductive when kept in comparable, water-free media.

On the other hand, the use of PAN-PVdF-Al$_2$O$_3$ gel membranes in fuel cell systems is expected to require an acid solution-fuel mixture inlet to maintain the acid concentration and therefore the proton flux throughout the cell. Figure 5 shows the current-voltage curve of a unoptimized, laboratory type fuel cell that uses the PAN-PVdF-Al$_2$O$_3$ gel membrane as the electrolyte, fed by an acid-methanol solution at the anode and by air at the cathode. Operating at room temperature and under constant air flux, the cell delivers a power density of about 2.0 mW cm^{-2} and a current of 20 mA cm^{-2}. These values are promising, and suggest that the PAN-PVdF-Al$_2$O$_3$ composite gel membranes may eventually be suitable for use in ambient temperature, direct methanol fuel cells; especially when one takes into account that in this preliminary work no attempt was made to optimize the MEA, and that a simple, in-house made, laboratory-type cell was used for the tests.

Conclusions

We show that a PAN-PVdF-Al$_2$O$_3$ composite blend is a suitable matrix to form gel-type, liquid acid

Fig. 4 Conductivity Arrhenius plot of a PAN-PVdF-Al$_2$O$_3$ composite membrane swollen by a 6 M H$_2$SO$_4$ aqueous solution. Relative external humidity ~0%
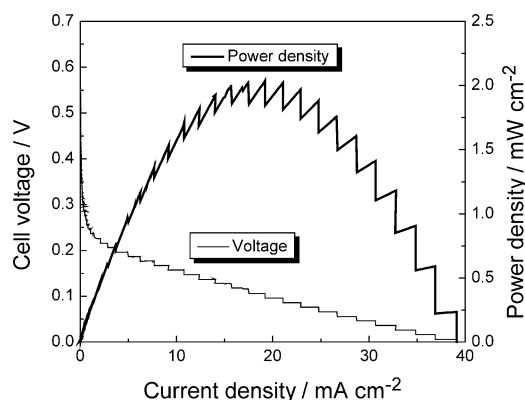

Fig. 5 Typical current-voltage curve for a PAN-PVdF-Al$_2$O$_3$ composite membrane in a methanol-air, laboratory-type fuel cell at room temperature. For the cell assembly see the "Experimental" section. Catalyst load: 3.2 mg cm^{-2} Pt. Electrode surface: 1.13 cm^2

solution-swollen, low cost, proton-conducting membranes. The results reported in this work demonstrate that these membranes have a high, stable conductivity characterized by a transport mechanism not critically affected by the external water content. In addition, good chemical stability is also expected from the use of fluoride-based polymers. All of these are promising features from the point of view of practical application. Indeed, preliminary tests, run in a unoptimized laboratory cell, suggest that these PAN-PVdF-based membranes are suitable separators for DMFCs, particularly those for portable devices.

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